J|A|C|S
COMMUNICATIONS

Published on Web 02/02/2006

PC Bond Cleavage of $(silox)_3NbPMe_3$ (silox = $^tBu_3SiO$) under Dihydrogen Leads to $(silox)_3Nb{=}CH_2$, $(silox)_3Nb{=}PH$ or $(silox)_3NbP(H)Nb(silox)_3$, and CH_4

Kurt F. Hirsekorn, Adam S. Veige, and Peter T. Wolczanski*

Department of Chemistry & Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853

Received November 14, 2005; E-mail: ptw2@cornell.edu

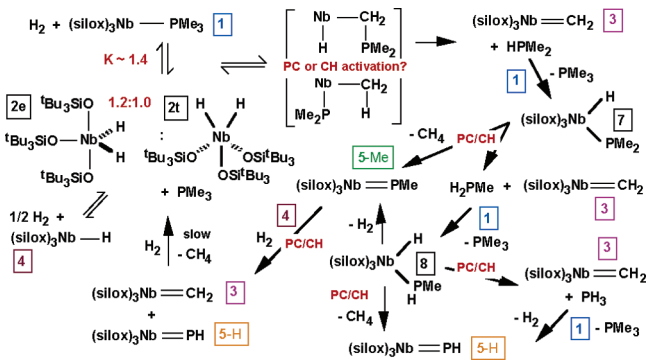
The formation of carbon−heteroatom bonds (e.g., PC bonds)[1−4] has been a focal point of organometallic reactivity studies for the past decade. Sometimes, it is also important to know how C−X bonds can be broken. Phosphorus−carbon bond cleavage, which is potentially useful with regard to the destruction of toxic agents, is often deleterious to transformations catalyzed by $((R/R')_3P)_nML_mX_o$. Substantial precedent exists for PR cleavage when R = aryl,[5−9] yet only a limited number of phosphorus−alkyl bond scissions are known,[10−15] and the majority involve chelating ligands (e.g., $Ph_2PCH_2Ph_2$).[14,15] While investigating the stability of $(silox)_3NbPMe_3$ (**1**)[16] under dihydrogen, we discovered that the PC bonds of PMe_3 were thermally severed, and that ambient light assisted the degradation. Herein we report our initial investigation of the thermal and light-dependent hydrogenation of PMe bonds.

When exposed to H_2 in hydrocarbon solvents, pseudo-T_d, indigo $(silox)_3NbPMe_3$ (**1**, $S = 1$) equilibrated ($K_{296} \sim 1.4$; $\Delta G° = -0.2$ kcal/mol) with two dihydrides, tbp $(silox)_3Nb(H_{eq})_2$ (**2e**) and pseudo-T_d $(silox)_3Nb(H_t)_2$ (**2t**), which were present in a 1.2:1.0 ratio. Scheme 1 reveals structures that are based on calculations of $(HO)_3NbH_2$ models (**2e′**, d(NbH) = 1.78 Å, d(H···H) = 3.11 Å; **2t′**, d(NbH) = 1.77 Å, d(H···H) = 1.92 Å), which are consistent with the rapid dissociative exchange of **2t** with H_2 ($k_f \sim 1.0(5)$ s^{-1}, $\Delta G^{‡}_{296} = 17.4(2)$ kcal/mol), and the greater width of its hydride resonance (**2t**, δ 14.08, $\nu_{1/2} \sim 160$ Hz; **2e**, δ 11.39, $\nu_{1/2} \sim 80$ Hz) in the ^1H NMR spectrum; quadrupolar broadening is expected to exert greater influence in the pseudo-cylindrically symmetric **2t**.[17]

Thermal (60 °C) degradation of **1** in the dark—with or without H_2 present—afforded ∼20% magenta $(silox)_3Nb{=}CH_2$ (**3**, ^1H ($^{13}C\{^1H\}$) NMR δ_{CH_2} 9.22 (216.35), $J_{CH} = 135$ Hz), which was alternately prepared via addition of $Ph_3P{=}CH_2$ to **1**.[18] In NMR tubes in ambient light (23 °C), PC bond cleavage occurred slowly without H_2, and ∼50% **3** formed over the course of 4 months along with a paramagnetic product tentatively identified as purple $(silox)_3NbH$ (**4**, ν(NbH/D) = 1730/1248 cm^{-1}), which was generated independently upon hydrogenation of $(silox)_3Nb$(olefin), ∼10% $(silox)_3Nb{=}PH$ (**5**-H, ^{31}P NMR δ 515.26, $J_{PH} = 75$ Hz), and CH_4. The addition of PH_3 to **1** cleanly provided **5**-H,[9,19] which was deprotonated with $LiN(SiMe_3)_2$ to generate the yellow phosphide[20−22] [$(silox)_3NbP$]-Li (**6**, ^{93}Nb NMR δ 463, d, $J_{NbP} \sim 550$ Hz; ^{31}P NMR δ 790, m, $\nu_{1/2} \sim 5800$ Hz)[23] in useful quantities.

In NMR tubes in ambient light, solutions of **1** + H_2 ⇄ **2e,t** + PMe_3, which were stable in the dark at 23 °C, produced a ∼4:3:1 ratio of $(silox)_3NbH$ (**4**):$(silox)_3Nb{=}CH_2$ (**3**):$(silox)_3Nb{=}PH$ (**5**-H) over 10 days along with methane. We conclude that **2e,t** has a greater light sensitivity toward PC bond cleavage than does **1**, and that its singlet excited states may be critical to facile PC activation. With a 450 W Hanovia (Hg) light source, PC bond cleavage diminished to ∼15%, and ∼80% **4** was generated after 3 days. Monohydride **4** appears to be thermodynamically favored, but independent reactions showed that it does not effect PC bond cleavage unless additional H_2 is present (**4** + 1/2H_2 ⇄ **2e,t**). The

Scheme 1



3:**5**-H ratio suggests that, upon initial activation of PMe_3, subsequent PC bond cleavages are swift (i.e., 4 **1** → 3 **3** + **5**-H + H_2).

Scale-up of the PC bond cleavage caused subtle changes in the product distribution. In a run monitored after 2 weeks, ∼10% $(silox)_3Nb{=}PH$ (**5**−H) was accompanied by ∼10% $(silox)_3Nb{=}$PMe (**5**-Me, ^{31}P NMR δ 553 (br)), a green component alternatively prepared from [$(silox)_3NbP$]Li (**6**) and MeI,[20] in addition to ∼40% $(silox)_3Nb{=}CH_2$ (**3**), and $(silox)_3NbH$ (**4**, ∼40%). In other reactions of 3 and 4 weeks, the **4**:**3**:**5**-H:**5**-Me ratio varied from 3:3.5:0:1.0 to 1.0:9.0:<0.5:0, respectively. Initial PC bond cleavage appears to depend on the reaction vessel (wall thickness), and thus the available UV light, but seems to be relatively insensitive to $[Nb]_{tot}$ and pH_2 (1−3 atm). In all instances, **5**-H grew in at the expense of **5**-Me, and CH_4 was produced—as much as 1.9 equiv after 2 weeks, and 2.7 equiv after 6 months according to Toepler pump measurements.

The ultimate loss of all three methyl groups from PMe_3 suggested a stepwise removal. Using the method of Abbayes et al.,[24] $HPMe_2$ and H_2PMe were prepared in situ and added to $(silox)_3NbPMe_3$ (**1**). With the former, a swift reaction afforded $(silox)_3HNbPMe_2$ (**7**), but **7** subsequently degraded ($t_{1/2} \sim 12$ h) to produce an initial ∼1:1 ratio of **3**:**5**-Me and CH_4. With H_2PMe, $(silox)_3HNbPHMe$ (**8**, $t_{1/2} \sim 30$ min) was generated, but precedented H_2 loss[9,19] predominated to give **5**-Me in 60% yield, whereas PC activation occurred to a lesser extent: 20% **5**-H, 20% **3**, and CH_4. The alkylphosphide hydrides[25,26] are likely resting states preceding PC or CH bond activation, and both demethylations occur on a time scale faster than that of the initial PC/CH bond activation of PMe_3. It is tempting to conclude that the **7** → **5**-Me transformation occurs via PC bond activation to give $(silox)_3MeNbPHMe$ (**7′**) followed by 1,2-MeH elimination, but one cannot rule out rearrangement of **7** via $(silox)_3HNbCH_2PHMe$ → $(silox)_3(H_2MeP)Nb{=}CH_2$ → **7′**.

A compilation of these observations is presented in Scheme 1. Light-facilitated oxidative addition of either a PC or CH bond[27] affords transients that are subject to 1,2-$HPMe_2$ elimination and formation of $(silox)_3Nb{=}CH_2$ (**3**). The degradation of $HPMe_2$ occurs via substitution of PMe_3 from **1** (or H_2 from **2e,t**) to give

10.1021/ja057747f CCC: $33.50

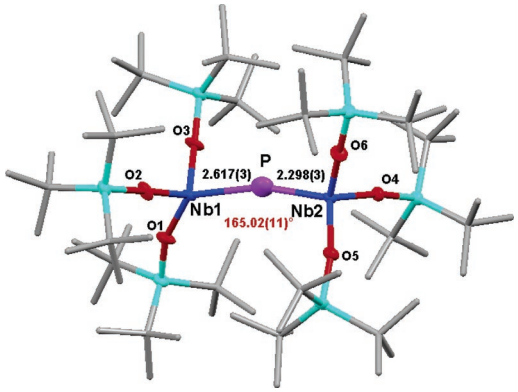


Figure 1. Molecular view and selected bond distances (Å) and angles (°) of $(silox)_3Nb{=}P(H)Nb(silox)_3$ (**9**): $d(NbO)_{av}$ = 1.904(12); O1−Nb1−O2 = 104.8(2), O1−Nb1−O3 = 102.3(2), O2−Nb1−O3 = 114.5(2), O1−Nb1−P = 135.7(2), O2−Nb1−P = 100.9(2), O3−Nb1−P = 98.9(2), O−Nb2−O_{av} = 108.1(10), and O−Nb2−P_{av} = 108.2(10).

$(silox)_3HNbPMe_2$ (**7**), which can be considered a source of $(silox)_3NbPHMe_2$. PC or CH bond activation and rearrangement, accompanied by 1,2-elimination of either CH_4 or H_2PMe, provides either $(silox)_3Nb{=}PMe$ (**5**-Me) or methylene **3**. Subsequent substitutions by H_2PMe on **1** or **2e,t** generate $(silox)_3HNbPMeH$ (**8**), a likely source of $(silox)_3NbPH_2Me$. Direct 1,2-elimination of H_2 affords **5**-Me, while another PC/CH activation step yields the methylene (**3**) and PH_3, thereby providing $(silox)_3Nb{=}PH$ (**5**-H) and H_2 as described above. **5**-Me was independently converted by PC/CH activation to **5**-H and **3** via the addition of $(silox)_3NbH$ (**4**) and H_2, which is a source of **2e,t**; its [Nb] dependence suggested a bimolecular PC/CH activation. Ultimately, a slow (4 weeks, 20% conversion) hydrogenation of $(silox)_3Nb{=}CH_2$ (**3**) regenerates **2e,t** along with CH_4, enabling hydrogenation of the remaining PMe_3. Surprisingly, when exposed to D_2, $(silox)_3Nb{=}CHD$ (**3**-d_1) and **3**-d_2 form more swiftly (2 weeks) than reductive elimination of the putative $(silox)_3NbD(CH_2D)$ intermediate.

When dihydrogen *and* dinitrogen ($pH_2 \sim pN_2$ = 175 Torr) were added to a solution of $(silox)_3NbPMe_3$ (**1**) in an NMR tube under ambient light, a brick red, insoluble precipitate formed. It was identified by an X-ray crystal structure as $(silox)_3Nb{=}P(H)Nb(silox)_3$ (**9**, Figure 1). Digestion of **9** in benzene-d_6 with ethylene present provided a 1:1 mixture of $(silox)_3Nb{=}PH$ (**5**−H) and $(silox)_3Nb(\eta\text{-}C_2H_4)$.[28] The $d(Nb^VP)$ of 2.298(3) Å is consistent with previous phosphinidenes (cf. $(silox)_3Ta{=}PPh$, 2.317(4) Å)[19] and is much shorter than the adjacent dative bond ($d(Nb^{III}P)$ = 2.617(3) Å), which is considerably longer than that of **1** (2.4923(7) Å).[16] The Nb^V center is pseudo-T_d, with $d(NbO)_{av}$ = 1.901(8) Å, ∠$ONbO_{av}$ = 108.1(10)°, and ∠$ONbP_{av}$ = 108.2(10)°, but the Nb^{III} core exhibits a modest angular distortion of electronic origin. The existence of an insoluble P-containing species helps explain why some "solutions" appear low in **5**-H and **5**-Me with respect to **3**.

$(silox)_3Nb{=}PH$ (**5**-H) needs to be hydrogenated or otherwise converted to regenerate **2e,t** for catalysis to occur.[29] High pressures of H_2 will aid in the conversion of $(silox)_3Nb{=}CH_2$ (**3**) to CH_4 and **2e,t**. We are currently exploring reaction conditions and the extension of these cleavage reactions to other phosphines.

Acknowledgment. We thank the NSF (CHE-0415506), Thomas R. Cundari, Rachel Combs (calculations), and Emil B. Lobkovsky (X-ray).

Supporting Information Available: Spectral and analytical data, CIF file for **9**, and experimental and computational procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Schwan, A. L. *Chem. Soc. Rev.* **2004**, *33*, 218−224.
(2) Moncarz, J. R.; Brunker, T. J.; Jewett, J. C.; Orchowski, M.; Glueck, D. S.; Sommer, R. D.; Lam, K. C.; Incarvito, C. D.; Concolino, T. E.; Ceccarelli, C.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2003**, *22*, 3205−3221.
(3) (a) Murata, M.; Buchwald, S. L. *Tetrahedron* **2004**, *60*, 7397−7403. (b) Gelman, D.; Jiang, L.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 2315−2318.
(4) Stradiotto, M.; Fujdala, K. L.; Tilley, T. D. *Helv. Chim. Acta* **2001**, *84*, 2958−2970.
(5) (a) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171−185. (b) DuBois, R. A.; Garrou, P. E.; Lavin, K. D.; Allcock, H. R. *Organometallics* **1986**, *5*, 460−466.
(6) (a) Bott, S. G.; Yang, K.; Richmond, M. G. *J. Organomet. Chem.* **2005**, *690*, 3067−3079. (b) Bott, S. G.; Shen, H. F.; Richmond, M. G. *J. Organomet. Chem.* **2004**, *689*, 3426−3437. (c) Bott, S. G.; Yang, K. Y.; Richmond, M. G. *J. Organomet. Chem.* **2004**, *689*, 791−800.
(7) (a) Geldbach, T. J.; Pregosin, P. S. *Eur. J. Inorg. Chem.* **2002**, *8*, 1907−1918. (b) Geldbach, T. J.; Pregosin, P. S.; Bassetti, M. *Organometallics* **2001**, *20*, 2990−2997.
(8) Grushin, V. V.; Marshall, W. J. *J. Am. Chem. Soc.* **2004**, *126*, 3068−3069.
(9) Fermin, M. C.; Ho, J.; Stephan, D. W. *Organometallics* **1995**, *14*, 4247−4256.
(10) Shin, J. H.; Parkin, G. *Chem. Commun.* **1998**, 1273−1274.
(11) (a) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Organomet. Chem.* **1990**, *394*, 417−432. (b) Snelgrove, J. L.; Conrad, J. C.; Yap, G. P. A.; Fogg, D. E. *Inorg. Chim. Acta* **2003**, *345*, 268−278.
(12) Nakajima, T.; Shimizu, I.; Kobayashi, K.; Koshino, H.; Wakatsuki, Y. *Inorg. Chem.* **1997**, *36*, 6440−6442.
(13) Lin, W.; Wilson, S. R.; Girolami, G. S. *Inorg. Chem.* **1994**, *33*, 2265−2272.
(14) Cotton, F. A.; Canich, J. A. M.; Luck, R. L.; Vidyasagar, K. *Organometallics* **1991**, *10*, 352−356.
(15) For recent examples, see: (a) Shiu, K.-B.; Jean, S.-W.; Wang, H.-J.; Wang, S.-L.; Liao, F.-L.; Wang, J.-C.; Liou, L. S. *Organometallics* **1997**, *16*, 114−119. (b) Doherty, N. M.; Hogarth, G.; Knox, S. A. R.; MacPherson, K. A.; Melchior, F.; Morton, D. A. V.; Orpen, A. G. *Inorg. Chim. Acta* **1992**, *200*, 257−270. (c) Katti, K. V.; Pinkerton, A. A.; Cavell, R. G. *Inorg. Chem.* **1991**, *30*, 2631−2633. (d) Lin, I. J. B.; Lai, J. S.; Liu, C. W. *Organometallics* **1990**, *9*, 530−531. (e) Elliot, D. J.; Holah, D. G.; Hughes, A. N.; Mirza, H. A.; Zawada, E. *Chem. Commun.* **1990**, 32−33.
(16) Veige, A. S.; Slaughter, L. M.; Lobkovsky, E. B.; Wolczanski, P. T.; Matsunaga, N.; Decker, S. A.; Cundari, T. R. *Inorg. Chem.* **2003**, *42*, 6204−6224.
(17) Cowan, B. *Nuclear Magnetic Resonance and Relaxation*; Cambridge University Press: London, 1997.
(18) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43−51.
(19) Bonanno, J. B.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1994**, *116*, 11159−11160.
(20) (a) Figureroa, J. S.; Cummins, C. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 984−988. (b) Figueroa, J. S.; Cummins, C. C. *J. Am. Chem. Soc.* **2004**, *126*, 13916−13917.
(21) (a) LaPlaza, C. E.; Davis, W. M.; Cummins, C. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2042−2044. (b) Cummins, C. C. *Chem. Commun.* **1998**, 1777−1786.
(22) Zanetti, N. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2044−2046.
(23) Wu, G.; Rovnyak, D.; Johnson, M. J. A.; Zanetti, N. C.; Musaev, D. G.; Morokuma, K.; Schrock, R. R.; Griffin, R. G.; Cummins, C. C. *J. Am. Chem. Soc.* **1996**, *118*, 10654−10655.
(24) Soulier, E.; Clément, J. C.; Yaouanc, J. J.; Abbayes, H. *Tetrahedron Lett.* **1998**, *39*, 4291−4294.
(25) Large $^2J_{PH}$ for **7** (^{1}H NMR δ 10.13, NbH, d, $^2J_{PH}$ = 151 Hz; ^{31}P NMR 160, br s, $\upsilon_{1/2}$ = 910 Hz) and **8** (^{1}H NMR δ 6.92, PH, ddq, $^1J_{PH}$ = 226 Hz, $^3J_{HH}$ = 5 Hz, $^3J_{HH}$ = 2 Hz, δ 11.59, NbH, dd, $^2J_{PH}$ = 114 Hz, $^3J_{HH}$ = 2 Hz; ^{31}P NMR δ 80, br s, $\upsilon_{1/2}$ = 530 Hz) suggests partial P···H bonding akin to the silyl-hydride/silane continuum. See: Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175−292.
(26) Leoni, P.; Pasquali, M.; Sommovigo, M.; Laschi, F.; Zanello, P.; Albinati, A.; Lianza, F.; Pregosin, P. S.; Rüegger, H. *Organometallics* **1993**, *12*, 1702−1713.
(27) (a) Rabinovich, D.; Zelman, R.; Parkin, G. *J. Am. Chem. Soc.* **1992**, *114*, 4611−4621. (b) Hascall, T.; Murphy, V. J.; Janak, K. E.; Parkin, G. *J. Organomet. Chem.* **2002**, *652*, 37−49.
(28) Hirsekorn, K. F.; Veige, A. S.; Marshak, M. P.; Koldobskaya, Y.; Wolczanski, P. T.; Cundari, T. R.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **2005**, *127*, 4809−4830.
(29) For an unusual catalytic PC bond cleavage, see: Khanna, P. K.; Jun, K. W.; Hong, K. B.; Baeg, J. O.; Mehrotra, G. K. *Mater. Chem. Phys.* **2005**, *92*, 54−58.

JA057747F